

JAPANESE

[JP,2000-154010,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL  
FIELD PRIOR ART EFFECT OF THE INVENTION  
TECHNICAL PROBLEM MEANS OPERATION  
EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

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**DETAILED DESCRIPTION**

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the rust-proofer also with a high effect whose safety to which the second [ an average of ] particle diameter makes an active principle 1 micrometer or less of particle zinc phosphate, its process, and this particle zinc phosphate by 1 micrometer or less in the primary particle diameter observed under the \*\*\* microscope is high.

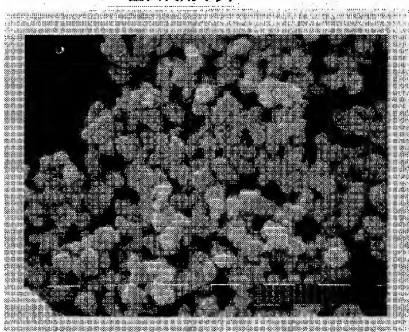
[0002]

[Description of the Prior Art]Conventionally, as a rust preventive pigment, lead compounds, such as chromium compounds, such as zinc chromate and strontium chromate, red lead oxide, basic lead chromate, and lead cyanamide, are used abundantly. However, since these chromium system rust preventive pigment and the lead system rust preventive pigment contain poisonous metal called chromium and lead during the presentation of a thing excellent in the rust prevention effect, from a viewpoint of safety, it is greatly considered as the problem in recent years.

[0003]Meanwhile, as a pollution-free and safe rust preventive pigment, its attention is paid to various phosphoric acid compounds, and it has changed so that especially zinc phosphate may be examined completely. Although zinc phosphate is used as a rust preventive pigment for many years, since the rust prevention effect is weak compared with chromium system rust preventive

Drawing selection **Drawing 1**

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pigments, such as zinc chromate, the actual condition is that the use range does not spread.

[0004]Several kinds of trials which atomize that particle are performed noting that it originates in the fault that the rust prevention effect of this zinc phosphate is weak having the large particle diameter which zinc phosphate originally has (particle diameter is set to tens of micrometers by a tabular crystal thing as for zinc phosphate.).

[0005]Although silica etc. are put into the reaction time of zinc phosphate, the trial which manufactures particle zinc phosphate is indicated and the trial which manufactures particle zinc phosphate by transposing the zinc of zinc phosphate to other metal is indicated by JP,4-310511,A at JP,49-2005,B, In the zinc phosphate obtained with such indication art, particle diameter is still large and particle zinc phosphate with a particle diameter of 1 micrometer or less is not created.

[Problem(s) to be Solved by the Invention]The purpose of a from book name has the second [ an average of ] particle diameter in providing as a pollution-free rust preventive pigment which develops 1 micrometer or less of particle zinc phosphate, and has the outstanding rust prevention effect in view of the above-mentioned actual condition.

[0006]

[Means for Solving the Problem]Particle zinc phosphate  $Zn_3(PO_4)_2$  and  $mH_2O$  (1) primary particle diameter seen under a

\*\*\*\* microscope obtained by an original process shown later as a result of inquiring wholeheartedly, in order that this invention persons may solve the above-mentioned problem is indicated to be with a following formula of 1 micrometer or less

(m found out among a formula () - a positive number, and that () - 4) could solve an aforementioned problem preferably.

[0007]The greatest feature of particle zinc phosphate of this invention is a point of particle zinc phosphate in which primary particle diameter has the uniform particle diameter of 1 micrometer or less so that more clearly than the after-mentioned electron microscope photograph.

[0008]This particle zinc phosphate with use of dry grinding and a dispersing agent, or wet milling. Mean particle diameter of secondary particle diameter can consider it as 1 micrometer or less of particle zinc phosphate easily, the secondary particle diameter D90 can set to 1 micrometer or less more preferably, and it is particle zinc phosphate which all the secondary particle diameter can set to 1 micrometer or less still more desirably. Since this particle zinc phosphate has fine particle diameter, when it is used as a rust preventive pigment of an anticorrosion paint, for example, It is hard to sediment and can make a uniform and precise coat generate, and since it is a submicron particle of 1 micrometer or less, solubility is also superior to usual zinc phosphate, A coat precise [ zinc phosphate ] and beautiful can be easily deposited in a surface of metal, and a rust prevention effect outstanding as a result can be given to a

surface of metal.

[0009]Primary particle diameter was a not less than 10-micrometer tabular crystal thing, conventional zinc phosphate sedimented easily, and that not only of a precise coat not being formed but solubility was bad, and it was difficult for it to also make an effective zinc phosphate coat form in a surface of metal. Such particle zinc phosphate of this invention was developed for the first time by an original process shown below.

[0010]Particle zinc phosphate of this invention can be obtained by the following processes.

[0011]Specifically, this particle zinc phosphate can be obtained by making a phosphoric acid compound and a zinc compound react in a drainage system medium under existence of organic acid. As a phosphoric acid compound, water soluble salts of phosphoric acid, such as orthophosphoric acid, pyrophoric acid, metaphosphoric acid, and polyphosphoric acid, these phosphoric acid, and alkaline metals, for example, phosphoric acid 1 sodium, disodium phosphate, phosphoric acid 3 sodium, etc. have preferred ammonium phosphate etc. As a zinc compound, a zinc oxide, zinc chloride, sulfate of zinc, zinc nitrate, zinc acetate, zinc hydroxide, etc. can be used, and there is no restriction in particular.

[0012]As organic acid, acetic acid, formic acid, propionic acid, butanoic acid, a valeric acid, caproic acid, Fatty acid monocarboxylic acid, such as enanthic acid, acrylic acid, crotonic acid, Aromatic monocarboxylic acids, such as unsaturation monocarboxylic acid, such as isocrotonic acid and undecylenic acid, and benzoic acid, Oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, Aliphatic dicarboxylic acid, such as suberic acid, azelaic acid, and sebacic acid, Aliphatic series unsaturated dicarboxylic acid, such as maleic acid and fumaric acid, phthalic acid, Dicarboxylic acid, such as aromatic dicarboxylic acid, such as isophthalic acid and terephthalic acid, and oxalacetic acid, Although polyvalent organic acid, such as tetracarboxylic acid, such as tricarboxylic acid, such as citrate, aconitic acid, D-isocitric acid, and malic acid, and ethylenediaminetetraacetic acid (EDTA), etc. are raised, polyvalent organic acid is desirable. Organic acid acts as crystallization inhibitor to a reaction of a zinc compound and a phosphoric acid compound, at a reaction under existence of this organic acid, crystallization is controlled, and a big crystal is not generated but zinc phosphate deposits as small particles. A kind or two sorts or more can be chosen and used for organic acid out of the above-mentioned organic acid, and the amount used is determined in consideration of a crystal grain child's size etc. to generate, is good to a zinc compound, and more preferably [ 0.5-10 mol% of ] desirable. [ 0.1-20 mol% of ] It is because it becomes the amount used superfluous for not influencing a size of a crystal in the range which zinc phosphate with a big crystal grain child exists, and exceeds 20-mol% in less than 0.1mol%. Before a reaction of a water-soluble-phosphate compound and a zinc compound, or

during a reaction, organic acid to apply can be added suitably. In order to be able to perform reaction temperature below 50 °C and to promote a reaction, stirring, supersonic vibration, etc. may be added.

[0013] Zinc phosphate which deposits under such a reaction condition is particles, and a primary particle observed with an electron microscope is 1 micrometer or less. This primary particle has a low condensation degree, and can be made into particle diameter near a primary particle comparatively easily by crack. After a reaction, if a dispersing agent is added to reaction mixture and also an addition rear stirrer gives strong stirring and wet milling for a dispersing agent before addition, it can dry and, specifically, can be considered as zinc phosphate of secondary particle diameter with a mean particle diameter of 1 micrometer or less which is particle diameter near a size of a primary particle after grinding. That is, it is a process of particle zinc phosphate which makes a phosphoric acid compound and a zinc compound react in a hydrophobic body under existence of organic acid, and subsequently adds a dispersing agent.

[0014] As an example of this dispersing agent, a higher fatty acid group, higher fatty acid salt, and the phosphoric ester of higher-fatty-acid system alcohol. Phosphoric acid and its salts, waxes, an anionic system surface-active agent, the Nonion system surface-active agent, a cation system surface-active agent, a both sexes active agent, or a coupling agent can be raised.

[0015] As higher fatty acid, for example Lauryl acid, pulmitic acid, oleic acid, Are stearic acid, capric acid, myristic acid, linolic acid, polycarboxylic acid, etc., and as higher fatty acid salt, For example, a salt or ammonium salt with an organic base, such as amines, such as a salt with alkaline metals, such as lithium salt of the above-mentioned higher fatty acid, sodium salt, and potassium salt, or dimethylamine, and diethylamine, etc. can be raised. As phosphoric ester of higher-fatty-acid system alcohol, For example, phosphoric ester, for example, lauryl ether phosphoric acid, of higher-fatty-acid alcohol, Alkyl ether phosphoric acid, such as stearyl ether phosphoric acid and oleyl ether phosphoric acid, Dialkyl ether phosphoric acid, alkylphenyl ether phosphoric acid, and dialkyl phenyl ether phosphoric acid. Or alkyl ether phosphates, such as oleyl ether sodium phosphate and stearyl ether potassium phosphate, hexametaphosphoric acid, its salts, etc. can be raised.

[0016] As an Nonion system surface-active agent, for example Palm-oil-fatty-acid monoethanolamide, Polyoxy alkylphenyl ether, such as ARUKIRORU/AMAIDO, such as lauryl acid diethanolamide, and polyoxyethylene alkyl phenyl ether, Polyoxyethylene alkyl ether, such as polyoxyethylene lauryl ether. Polyethylene glycol fatty acid ester, such as a distearic acid polyethylene glycol. Sorbitan fatty acid ester species, such as monocapric acid sorbitan, monostearin acid sorbitan, and distearic acid sorbitan, Polyoxyethylene sorbitan fatty acid ester, such as monostearin acid polyoxyethylene sorbitan,

polyoxyethylene sorbitol fatty acid ester, polyoxyethylene polyoxypropylene alkyl ether, and glycol ether can be raised.

[0017]As a cation system surface-active agent, for example Chloridation lauryl trimethylammonium, Alkyl trimethylammonium salts, such as a cetyltrimethylammonium bromide and stearyl chloride trimethylammonium, Alkyldimethyl benzylammonium salts, such as stearyldimethylbenzylammonium chloride, a benzalkonium chloride, and a chloridation lauryldimethyl benzylammonium salt, etc. can be raised.

[0018]As a both sexes active agent, alkyl betaines, such as a palm oil alkyl betaine. Glycines, such as imidazoline, such as alkylamide betaines, such as lauryldimethyl betaine aminoacetate, and a Z-alkyl N-carboxymethyl N-hydroxyethyl imidazo ream betaine, and a polio KUCHIRUPORI aminoethyl glycine, can be raised.

[0019]As a coupling agent, the Silang system coupling agent, an aluminate coupling agent, a titanium system coupling agent, a zirconium system coupling agent, etc. can be raised, for example. In this invention, one or more sorts chosen from the above-mentioned dispersing agent can also be used simultaneously.

[0020]An addition of a dispersing agent is 0.1 to 10 % of the weight, and is 0.5 to 6% of the weight of a range preferably. At 0.1 or less % of the weight, dispersibility is bad, and it is not economically advantageous although 10 % of the weight or more is enough as an effect.

[0021]

[Function]Thus, especially when using it as various rust-proofers, such as rustproof coating fluid containing a paint and a rust preventive pigment, the particle zinc phosphate of obtained this invention does not have restriction, and can be used in accordance with a conventional method. Since the particle zinc phosphate of this invention can be cracked to the particle diameter near a primary particle simple by a ball mill, a sand mill, etc. which are used when usually manufacturing these liquefied articles especially when using it for liquefied articles, such as a paint and rustproof coating fluid, a rust prevention effect can be acquired easily. The particle zinc phosphate of this invention is the strong point also with big particle diameter being also uniform. When it blends with a paint, a rust-proofer, etc., it is stabilized and a uniform coat can be obtained.

[0022]The rust-proofer which consists of zinc phosphate of this invention can carry out [ paint ]-izing using various paint resin, such as an oil system, a solvent system, an aqueous system, and an emulsion system, etc. Specifically, for example Alkyd resin, phenol resin, amino resin, Rubber derivatives, such as oil system resin, such as various synthetic resins for paints, such as an epoxy resin, urethane resin, polyvinyl resin, an acrylic resin, a fluoro-resin, silicone resin, and polyester resin, oil varnish, and boiled oil, chlorinated rubber, and cyclized rubber, cathodic electrodeposition resin, and other fibrin derivatives are used.

These resin can be independent, or can be used together two or more sorts, and can also be used.

[0023]The rust-proofer of this invention has a white color tone, and can choose color freely.

[0024]The following examples are shown in order to clarify this invention more.

[Example]

[0025]The water 180g was put into 1500 ml of examples stainless steel container, and the bottom zinc oxide 50g of stirring and the citrate 1 hydrate 3.87g were added, and it mixed. The 75% phosphoric acid 53.5g was made to add and react to this mixed liquor over 30 minutes.

Subsequently, after filtering this reaction mixture by the nutsche and fully washing it with water in accordance with a conventional method, it dried and ground at 110 °C for 12 hours, and the white powder 83.6g was obtained. This powder was observed under the 4000x microscope. The result was as being shown in [drawing 1](#) (4000x microphotograph). From this result, it is checked that primary particle diameter is 1 micrometer or less.

[0026]Except having added the hexametaphosphoric acid sodium solution 8.6g 10% as a dispersing agent, into the mixed liquor of example 2 Example 1, treating operation was performed like Example 1, and the white powder 82.1g was obtained into it. When particle size distribution was measured for this powder using the laser establishment type size distribution measuring device (the Shimadzu make, SALD-2000A), the mean particle diameter D50 was 0.95 micrometer.

[0027]Except having added the polycarboxylic acid ammonium solution 8.6g 10% as a dispersing agent, into the mixed liquor of example 3 Example 1, treating operation was performed like Example 1, and the white powder 82.9g was obtained into it. The mean particle diameter D50 of this powder was 0.92 micrometer.

[0028]Wet milling was carried out to the mixed liquor of example 4 Example 1 using the bowl mill pulverizer (φ10.5-mm zirconia beads). In this liquid, 8.6g of sodium polycarboxylate solution was added 10%, it processed like Example 1 succeeding in it, and the white powder 80.6g was obtained in it. The mean particle diameter D50 of this powder was 0.74 micrometer.

[0029]White powder was obtained like Example 1 except not adding comparative example 1 citrate. This powder was observed with the electron microscope. The result was as being shown in [drawing 2](#) (electron microscope photograph). From this result, many not less than 10-micrometer things are accepted for a primary particle.

[0030]

[Effect of the Invention]The primary particle diameter which observed the particle zinc phosphate of this invention under the 4000x microscope is [ the second / an average of / particle diameter ] 1 micrometer or less of particle zinc phosphate in 1 micrometer or less.

If this particle zinc phosphate is used as a rust preventive pigment, safety can provide the anticorrosion paint and rust-

proofer in which it is high and an effect is also high.  
The particle zinc phosphate of this invention has the good dispersibility in the inside of a paint, and is [ that are hard to sediment and it is hard to make a coat produce nonuniformity ] useful to the rust-proofer for paints at \*\*.

[Translation done.]